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(54) Title: PRODUCTION OF VINYLIC POLYMERS			
(57) Abstract			
<p>A method of producing an acrylic polymer by atom transfer radical polymerisation (ATRP) which comprises the steps of: (i) forming a mixture of at least one vinylic monomer, a transition metal complex or precursor thereof, wherein the transition metal in a first oxidation state is reversibly capable of bonding to a halogen atom X and entering a second oxidation state; (ii) adding to said mixture an initiator R-X, where X is a halogen and R is an alkyl, substituted alkyl or halogenated carbon group, such that the acrylic monomer is polymerised by atom transfer radical polymerisation; characterised in that said mixture in stage (i) further comprises a Lewis acid which is soluble in the reaction mixture. The method produces faster reactions than conventional ATRP methods.</p>			

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Production of vinylic polymers

The present invention concerns the production of vinylic polymers, especially, but not limited to, acrylic polymers, for example methacrylate and acrylate copolymers and homopolymers, using atom transfer radical polymerisation.

5 Atom transfer radical polymerisation (ATRP) of unsaturated monomers such as styrene and methyl methacrylate has been reported by Matyjaszewski et al (*J. Am. Chem. Soc.*, (1995), 117, 5614; *J. Am. Chem. Soc.*, (1997), 119, 674; *Macromolecules*, (1998), 31, 1527) and Haddleton et al (*Macromolecules*, (1997), 30, 2190; *Macromolecules*, (1997), 30, 3992). It is a method of living free radical polymerisation which is initiated by the

10 abstraction of a halogen atom from an alkyl halide by a stabilised metal complex (usually copper or ruthenium) to produce an alkyl radical. The alkyl radical then adds to the monomer in a chain reaction which may be terminated by the addition of an abstracted halogen back from the metal complex. Subsequent removal of the halogen may then lead to further addition of monomer. This mode of polymerisation is controlled and normally

15 leads to halogen-terminated polymer of narrow molecular weight distribution in which the molecular weight is dependent upon the concentration of initiator used.

One problem which has been found with ATRP polymerisation reactions is that they proceed at rates which are often unattractive commercially. The present invention provides an ATRP process which differs from the standard process.

20 Sawamoto et al (*Macromolecules* (1995) 28 1721 - 1723) describe the use of a particular Lewis acid, methyl aluminium bis (2,6-di-*tert*-butyl-4-methyl) phenoxide ((MeAl(ODBP)<sub>2</sub>), in an ATRP reaction to polymerise methyl methacrylate (MMA) using dichlorotris(triphenylphosphine)ruthenium(II) and carbon tetrachloride initiator. He found that the MeAl(ODBP)<sub>2</sub> was an essential part of the initiator system because it activated

25 the CCl<sub>4</sub> initiator to form radicals. The reaction is ineffective in the absence of the MeAl(ODBP)<sub>2</sub> compound.

We have unexpectedly found a process for producing polymer by ATRP methodology which shows an increased reaction rate compared to known ATRP reactions.

According to the invention, we provide a method of producing an acrylic polymer which comprises the steps of

- (i) forming a mixture of at least one vinylic monomer, a transition metal complex or precursor thereof, wherein the transition metal in a first oxidation state is reversibly capable of bonding to a halogen atom X and entering a second oxidation state;
- (ii) adding to said mixture an initiator R-X, where X is a halogen and R is an alkyl, substituted alkyl or halogenated carbon group, such that the acrylic monomer is polymerised by atom transfer radical polymerisation;

characterised in that said mixture in stage (i) further comprises a Lewis acid which is

10 soluble in the reaction mixture.

The at least one vinylic monomer preferably comprises an acrylic monomer such as an alkyl acrylate, alkyl (alkyl)acrylate or acrylic or (alkyl)acrylic acid. Preferred monomers include optionally functionalised alkyl acrylates and alkyl methacrylates, especially, methyl methacrylate (MMA), ethyl methacrylate, n-propyl methacrylate, t-butyl methacrylate, t-butyl methacrylate, hydroxyethyl methacrylate, ethyl acrylate, butyl acrylate, methyl acrylate. Other suitable monomers include styrene (including substituted or functionalised styrenes) acrylonitrile and other vinylic species, e.g. vinyl acetate.

The transition metal which forms a complex or precursor thereof, wherein the transition metal in a first oxidation state is reversibly capable of bonding to a halogen atom X and

20 entering a second oxidation state, may be selected from e.g. copper, nickel, iron or ruthenium but is preferably copper. The transition metal complex may be any of those which have been found suitable for use in ATRP reactions of vinylic monomers, e.g. as described in the literature references supra. The transition metal complex preferably comprises Cu-L<sub>n</sub>, where L is a ligand which is preferably a substituted pyridine compound,

25 especially 2,2'-bipyridine or a substituted analogue thereof. Suitable substituted 2,2'-bipyridines include 4,4'-di-(alkyl)-2,2'-bipyridines where the alkyl group comprises a C<sub>1-20</sub> alkyl group such as t-butyl, n-heptyl, 5-nonyl or other bulky group. Such complexes may be formed in situ by the reaction of a copper (I) halide with the ligand. The Cu halide is preferably CuCl or CuBr but can also be Cu(I). n is normally 1 -3, especially 2.

30 Preferably the molar ratio of Cu : ligand is about 1:2, e.g. 1:1.8 - 2.2. Other suitable transition metal complexes include Ru(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as described by Sawamoto et al (*Macromolecules* (1995) 28 1721 - 1723).

The initiator is a halogen-containing compound R-X. The halogen X is preferably Cl or Br. Suitable initiator compounds include alkyl and aryl halides and other organic halide compounds such as ethyl-2-bromo isobutyrate, 1-phenylethyl bromide, 1-phenylethyl chloride, *p*-toluenesulphonyl chloride, benzhydryl chloride, 1,1,1-trichloroacetone, 5  $\alpha,\alpha$ -dichloroacetophenone, carbon tetrachloride.

We have unexpectedly found that the addition of a Lewis acid to the reaction medium significantly increases the rate of ATRP reactions. Preferred Lewis acids include aluminium complex compounds, metal halides, e.g. Zinc halides, lithium halides, iron trichloride, boron trifluoride, acetyl acetonate (Acac), conjugated organic acids and other 10 organic acids such as camphorsulfonic acid. A preferred aluminium compound is methyl aluminium bis (2,6-di-*tert*-butyl-4-methyl) phenoxide. The Lewis acid should be soluble in the reaction medium.

When the ATRP reaction is carried out by the method of the invention, i.e. in the presence of a Lewis acid compound, the reaction rate may be increased to the extent that the 15 reaction solution becomes viscous much more quickly than in the absence of such a compound. In these circumstances, control over the polydispersity of the polymer produced may be adversely affected, possibly because of the impaired mobility of the polymer chains, and/ or other reactant or intermediate species present. We have found that the detrimental effects of a rapid rise in the viscosity of the reaction mixture may be 20 overcome to a large extent by the addition of solvent to the reaction mixture as the reaction progresses.

In a second aspect of the invention we provide a method of producing an acrylic polymer which comprises the steps of

- (i) forming a solution of at least one vinylic monomer, a solvent and a transition metal 25 complex or precursor thereof, wherein the transition metal in a first oxidation state is reversibly capable of bonding to a halogen atom X and entering a second oxidation state;
- (ii) adding to said mixture an initiator R-X, where X is a halogen and R is an alkyl, substituted alkyl or halogenated carbon group, such that the acrylic monomer is polymerised by atom transfer radical polymerisation;
- 30 characterised in that said mixture in stage (i) further comprises a Lewis acid which is soluble in the reaction mixture and in that an additional quantity of solvent is added to the

reaction mixture after stage (ii) when at least a part of the acrylic monomer has been polymerised.

The addition of the additional solvent preferably occurs gradually, e.g. dropwise or in portions over time. By additional solvent we mean a quantity of solvent which is not present in the reaction mixture before the initiator is added. The solvent is preferably the same chemically as the solvent used to form the solution of reactants in stage (i). Suitable solvents include ethyl acetate, *o*-xylene etc.

The reaction mixture may also include a chain transfer agent such as a mercaptan or a catalytic chain transfer compound. Such compounds are known in the art. Suitable mercaptans include alkyl mercaptans which have at least one functional -S-H group which are known in the art as chain transfer agents, in particular for use in acrylic polymers. Examples of suitable mercaptans include butyl mercaptan, nonyl mercaptan, dodecyl mercaptan and others.

The amount of chain transfer agent added to the reaction mixture varies according to the type of substance used and its mode of action. If a catalytic chain transfer agent (CCT) is used, we have found that the optimum properties of the resulting polymer are achieved when the CCT is present at a level of 3 - 30, more preferably 5 - 15, especially about 10 ppm by weight based on the total weight of the reaction mixture, including solvent. When a mercaptan is used it is preferably present at a molar concentration of active sites approximately equal to the molar concentration of the initiator used. This is because each initiator molecule may initiate one chain and each mercaptan group may terminate one chain.

The reaction mixture may contain other additives which are used to change the properties of the polymer, e.g. impact-modifying materials, colourants, processing aids etc.

25 The invention will be further described in the following examples.

Example 1

Method of producing polymethyl methacrylate by ATRP

All reactant concentrations are given in mol dm<sup>3</sup> (M) of the total reaction mixture. The ATRP polymerisation was conducted as follows:

46.7 mM Copper(I)bromide ( $\text{Cu(I)Br}$ ) and 141 mM 2,2'-bipyridine (bpy) and 23.9 mM of a Lewis acid (if used) were introduced to a 100 ml round-bottomed flask fitted with a sidearm condenser and oxygen was removed by three successive vacuum-nitrogen purges. 5.1 M of ethyl acetate and 4.67 M MMA were then added using dry glass syringes. The resultant mixture was then heated with stirring, under an atmosphere of dry nitrogen, to 90°C before addition of 23.9 mM ethyl-2-bromoisobutyrate (EBIB) initiator via a dry glass Hamilton syringe. The temperature of the reaction mixture was monitored throughout and maintained at 90 °C. The initial ratios of  $[\text{Cu(I)Br}]_0 : [\text{bpy}]_0 : [\text{initiator}]_0 = 2:6:1$ .

The PMMA produced in this way was isolated by resuspension of the reaction mixture in tetrahydrofuran (Fisher) followed by filtration through a small column of alumina (activated, Brockmann I, 58Å, Aldrich) to remove excess Cu, and finally precipitation into hexane (Fisher). The polymer was analysed by X-ray fluorescence which showed that the Cu content of the PMMA product was <20 ppm. Conversion was determined gravimetrically after the polymer had been dried in a vacuum oven at 80°C for 3 h.

All reactions were performed using the method described in Example 1, except where noted below.

Example No	Lewis acid	Reaction time (h)	$M_n$	$M_w/M_n$	% conv.
1	$\text{AlMe(OMDPB)}_2$	2.0	17,300	1.8	92
2 (comp)	NONE	16	22,500	1.3	95
3	$\text{AlMe(OMDPB)}_2$	2.0	17,300	1.4	80
4	$\text{ZnBr}_2$	2.5	18,300	1.9	68
5	$\text{ZnBr}_2$	2.0	22,400	1.8	75
6	$\text{ZnBr}_2$	3.0	18,300	1.7	72
7	$\text{LiBr}$	2.5	19,400	1.8	78
8	$\text{LiCl}$	2.0	18,200	1.4	61
9	Camphorsulfonic acid	3.0	21,100	1.7	75
10	Acac	3.0	18,800	2.0	83

### Example 3

30 ml of additional EtOAc solvent was added dropwise to the reaction after 30 minutes for the remaining 90 minutes of reaction time in order to counteract the rapid increase in viscosity as the reaction progressed.

Example 5

The concentration of Cu(I)Br was 93.4 mM in this Example.

Example 6

This reaction used *o*-xylene as a solvent and the reaction was done at a temperature of  
5 120 °C

**Claims**

1. A method of producing an acrylic polymer which comprises the steps of
  - (i) forming a mixture of at least one vinylic monomer, a transition metal complex or precursor thereof, wherein the transition metal in a first oxidation state is reversibly capable of bonding to a halogen atom X and entering a second oxidation state;
  - (ii) adding to said mixture an initiator R-X, where X is a halogen and R is an alkyl, substituted alkyl or halogenated carbon group, such that the acrylic monomer is polymerised by atom transfer radical polymerisation;

characterised in that said mixture in stage (i) further comprises a Lewis acid which is soluble in the reaction mixture.

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2. A method as claimed in claim 1, wherein said Lewis acid is selected from the group comprising aluminium complex compounds, metal halides, acetyl acetonate, conjugated organic acids and other organic acids such as camphorsulfonic acid

3. A method of producing an acrylic polymer which comprises the steps of
  - (i) forming a solution of at least one vinylic monomer, a solvent and a transition metal complex or precursor thereof, wherein the transition metal in a first oxidation state is reversibly capable of bonding to a halogen atom X and entering a second oxidation state;
  - (ii) adding to said mixture an initiator R-X, where X is a halogen and R is an alkyl, substituted alkyl or halogenated carbon group, such that the acrylic monomer is polymerised by atom transfer radical polymerisation;

characterised in that said mixture in stage (i) further comprises a Lewis acid which is soluble in the reaction mixture and in that an additional quantity of solvent is added to the reaction mixture after stage (ii) when at least a part of the acrylic monomer has been polymerised.

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## INTERNATIONAL SEARCH REPORT

Int	ional Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F4/00

According to International Patent Classification (IPC) or to both national classification and IPC
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B. FIELDS SEARCHED
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Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
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C. DOCUMENTS CONSIDERED TO BE RELEVANT
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Category <sup>a</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 872 493 A (UNIV CASE WESTERN RESERVE)  21 October 1998 (1998-10-21)</p> <p>claims 1,7-9  page 3, line 57  page 4, line 2-15  page 4, line 40-56  page 5, line 49  examples 1-4</p> <p>---</p> <p style="text-align: center;">-/-</p>	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Int'l. Appl. No.
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C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 763 548 A (MATYJASZEWSKI KRZYSZTOF ET AL) 9 June 1998 (1998-06-09) column 25, line 10-27 claims 1,6,8,9 example 1 column 5, line 52-58 column 8, line 23-47 column 9, line 47-53 column 10, line 1,45 column 18, line 52-54 _____	1-3
A	CHEMICAL ABSTRACTS, vol. 132, Columbus, Ohio, US; abstract no. 166605, GUO, JIANHUA ET AL: "Catalytic system including Al(O <i>i</i> Pr) <sub>3</sub> as a promoter for atom transfer radical polymerization" XP002138470 abstract & GAOFENZI XUEBAO (1999), (6), 725-730 , _____	1-3

## INTERNATIONAL SEARCH REPORT

## Information on patent family members

Int'l. Application No.  
PCT/GB 00/00324

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0872493	A 21-10-1998	US 5886118 A		23-03-1999
		AU 700083 B		24-12-1998
		AU 5948398 A		29-10-1998
		CA 2232645 A		14-10-1998
		CN 1211580 A		24-03-1999
		JP 10324703 A		08-12-1998
		ZA 9802564 A		06-01-1999
US 5763548	A 09-06-1998	AU 5306996 A		16-10-1996
		BR 9604887 A		30-11-1999
		CA 2216853 A		03-10-1996
		CN 1183107 A		27-05-1998
		EP 0817806 A		14-01-1998
		JP 10509475 T		14-09-1998
		WO 9630421 A		03-10-1996